

Quantum Approach to a Derivation of the Second Law of Thermodynamics

Jochen Gemmer, Alexander Otte and Günter Mahler

*Institut für Theoretische Physik,
Universität Stuttgart, Pfaffenwaldring 57,
70550 Stuttgart, Germany*

We re-interpret the microcanonical conditions in the quantum domain as constraints for the interaction of the “gas-subsystem” under consideration and its environment (“container”). The time-average of a purity-measure is found to equal the average over the respective path in Hilbert-space. We then show that for typical (degenerate or non-degenerate) thermodynamical systems almost all states within the allowed region of Hilbert-space have a local von Neumann-entropy S close to the maximum and a purity P close to its minimum, respectively. Typically thermodynamical systems should therefore obey the second law.

The second law has been formulated in a number of different ways [1]: According to Clausius’ postulate heat cannot flow spontaneously from a colder to a hotter system. Thomson’s formulation reads: “It is impossible to construct a perpetuum mobile of the second kind.” Such rules define, essentially, some sort of irreversibility, i.e. the existence of a state function usually called entropy, S , which can only increase in closed systems. The second law is arguably one of the most fundamental and far-reaching laws of physics; nevertheless its origin remains puzzling.

On the macroscopic level the second law enables us to calculate state equations from the requirement that entropy has to be maximized under the condition of given extensive variables in order to get a thermodynamical potential as a function of those.

On the microscopic level irreversibility comes in conflict with the notorious reversibility of all fundamental physical laws. It has been the challenge for statistical mechanics to reconcile $dS/dt \geq 0$ with the underlying microscopic dynamics.

Irreversibility in classical mechanics is conventionally introduced via two different schemes (cf. [3]): The Boltzmann approach, based on the hypothesis of molecular chaos (*Stosszahlansatz*) and the Gibbs ensemble approach, based on the hypothesis of quasi-ergodicity. Both these attempts have to acknowledge some additional assumptions which do not follow from the underlying microscopic laws.

This fact has led to continuing controversies as to whether this situation can be the last word. Several researchers suggested quantum mechanics as a possible remedy.

L. D. Landau and E. M. Lifshitz [4] expected that quantum measurements – making a difference between future

and past – should be responsible for the entropy increase according to the second law. This assertion has never been proved, though.

E. Schrödinger [5] argued that the conventional canonical distributions of thermodynamics can be obtained also for a system described by a single wavefunction, if one invokes “the old crux of molecular disorder”.

J. von Neumann [3] was able to show that a non-degenerate system should, indeed, obey a quantum-mechanical version of ergodicity under fairly weak conditions. In addition he felt obliged to introduce “macroscopic observers” (coarse graining) in order to come into contact with standard thermodynamics.

This latter aspect has then been taken up also by W. Pauli and M. Fierz [6]. These authors insisted that the 2nd law should be explained without reference to external perturbations like those induced by quantum measurements.

G. Lindblad [7] observed that the entropy of a multipartite system defined as the sum of the respective partial entropies of the subsystems would tend to increase due to the neglect of correlations (entanglement). This fact could be taken as a quantum mechanical justification of Boltzmann’s *Stosszahlansatz*.

W. Zurek [8] and his coworkers have discussed in great detail how the interaction of a quantum system with its environment may induce quasi-classical behavior in the former (“environment-induced superselection rules”). They argued that the second law should eventually result from the impossibility of isolating macroscopic systems from their environment [9].

Many of these ideas are pertinent to our present investigation. It is the purpose of this Letter to show that under (appropriately redefined) microcanonical conditions the second law of thermodynamics follows from a quantum mechanical analysis of the total system partitioned into the object and the environment.

A purity measure that is formulated within standard quantum mechanics but has also an interpretation within thermodynamics is the von Neumann-entropy

$$S(\hat{\rho}) := -k \text{Tr} \{ \hat{\rho} \ln \hat{\rho} \}. \quad (0.1)$$

If this entropy is zero, the system is in a pure state, if it takes on its maximum value $S_{max} = k \ln(N)$, where N is the system size (number of accessible states), the system is in the maximally mixed state. Another measure is the “purity” P :

$$P(\hat{\rho}) := \text{Tr} \{ \hat{\rho}^2 \}. \quad (0.2)$$

If P takes on its maximum value 1 the system is in a pure state, if P takes on its minimum value $\frac{1}{N}$ the system is in the maximally mixed state.

For those extreme cases the two measures uniquely map onto each other. For general cases, however, this does not hold true anymore. Nevertheless, states with $P(\hat{\rho}) \approx 1$ will have $S(\hat{\rho}) \approx 0$ and states with $P(\hat{\rho}) \approx P_{min}$ will have $S(\hat{\rho}) \approx S_{max}$. In the following we mainly consider P and get back to S in the end.

Using the von Neumann-equation for the density operator of the total system it can easily be shown that the entropy and the purity of a closed system that does not interact with any other system are conserved.

This fact might be considered a contradiction to the second law which demands that entropy should be maximized during the evolution of a closed system.

If the full system is being regarded as divided into two subsystems (I and II), the reduced density operators are:

$$\hat{\rho}_I = \text{Tr}_{II} \{\hat{\rho}\}, \quad \hat{\rho}_{II} = \text{Tr}_I \{\hat{\rho}\} \quad (0.3)$$

Entropy and purity may be defined for each subsystem as before, using $\hat{\rho}_I$ ($\hat{\rho}_{II}$) instead of $\hat{\rho}$.

Since those are not the density operators that appear in the von Neumann-equation, S_I (S_{II}) and P_I (P_{II}) defined on basis of these operators are no longer conserved. Those are the quantities we are going to examine.

Although the following ideas apply to all sorts of subsystems, we want to refer to the system of which the entropy is to be calculated as the “gas-system”, g , and all the surrounding as the “container-system”, c .

The full Hamiltonian is now divided according to the same scheme:

$$\hat{H} =: \hat{L}_g + \hat{L}_c + \hat{W} \quad (0.4)$$

\hat{L}_g describes the energies arising from the gas particles alone, including their mutual interactions. \hat{L}_c describes the corresponding energies of the container particles alone. \hat{W} describes the interaction terms that depend on both, the coordinates of gas particles and the container particles. These are here basically the “wall” interactions that keep the gas particles inside the container.

The energy eigenstates of a free gas are unbound and continuous. It is far more convenient to have bound states for the “separate” systems. Thus we modify the Hamiltonian formally in the following way:

$$\hat{H} =: \hat{L}'_g + \hat{L}_c + \hat{W}' \quad (0.5)$$

with

$$\hat{L}'_g := \hat{L}_g + \hat{V} \quad \text{and} \quad \hat{W}' := \hat{W} - \hat{V} \quad (0.6)$$

where \hat{V} models the mean effect of the container on the gas particles. \hat{V} is an effective potential that only depends on the coordinates of the gas particles and is chosen to minimize \hat{W}' . Usually the container is simply modelled

by some “box” potential \hat{V} , neglecting \hat{W}' altogether. But however small, starting from first principles \hat{W}' will always be present, and represents a coupling.

We consider the gas-system to be closed in the thermodynamical sense, i. e., controlled by microcanonical conditions ($E, V, N = \text{const.}$); this is clearly an idealization but can routinely be realized in an approximate way.

A system that is closed on the macroscopic level (thermodynamically closed) does not need to be closed on the microscopic (quantum-) level (i. e. not interacting with any other system).

The fact that no extensive quantities are to be exchanged, however, puts constraints on its Hamiltonian, especially on the interactions a system can have with its surrounding, in order for it to be thermodynamically closed.

The strict conservation of particles N is taken into account simply by the way the system is partitioned. To which accuracy the volume V stays fixed is set by \hat{L}_c . Microcanonical conditions then correspond to a box with very high, in the limit of the volume V being exactly conserved, infinitely high potential walls.

The condition that no energy is to be exchanged further constrains the Hamiltonian. The energy contained in the gas is given by:

$$E_g := \langle \hat{L}'_g \rangle. \quad (0.7)$$

If this is to be conserved, it follows that

$$[\hat{L}'_g, \hat{H}] = 0 \quad [\hat{L}'_g, \hat{W}'] = 0. \quad (0.8)$$

Except for these constraints we need not specify \hat{W}' in more detail.

Based on these commutator relations we find that for any energy eigenspace A, B

$$\sum_{i,j} |\psi_{ij}^{AB}(t)|^2 = \sum_{i,j} |\psi_{ij}^{AB}(0)|^2 \quad (0.9)$$

is a conserved quantity, set by the initial state, where ψ_{ij}^{AB} denotes the amplitudes of the degenerate product energy eigenstates of $\hat{L}'_g + \hat{L}_c$ (“ i ” denoting the gas, “ j ” the container part of the product) that are associated with the energy eigenvalues $E_A^g(E_B^c)$ in the gas-(container-) system.

Since we want to consider cases here that have zero local entropy in the beginning (product states), we get

$$\sum_{i,j} |\psi_{ij}^{AB}(0)|^2 = \sum_{i,j} |\psi_i^A(0)|^2 |\psi_j^B(0)|^2 = P_A^g P_B^c \quad (0.10)$$

where $P_A^g(P_B^c)$ are the probabilities of finding the gas-(container-) system somewhere in the possibly highly degenerate subspace characterized by the energy eigenvalues $E_A^g(E_B^c)$. If no energy is to be exchanged, clearly these probabilities have to remain conserved. This is the constraint that microcanonical conditions impose on the accessible region of Hilbert-space.

Although we are interested in $P(t \rightarrow \infty)$, we start by considering the time average of the purity P for reasons that will become clear later.

$$\bar{P} := \frac{1}{T} \int_0^T P(|\psi(t)\rangle) dt \quad (0.11)$$

Choosing a special parametrization for $|\psi\rangle$, we can convert the time integral into an integral over the trajectory generated by the total system's dynamics for given initial conditions. Parametrizing $|\psi\rangle$ in terms of the real and imaginary parts of its amplitudes

$$|\psi(t)\rangle := \{\psi_{ij}(t), \psi'_{ij}(t)\} \quad (0.12)$$

we can write instead of (0.11)

$$\bar{P} = \frac{\int_{|\psi(0)\rangle}^{|\psi(T)\rangle} P(\{\psi_{ij}, \psi'_{ij}\}) \frac{1}{v_{eff}} |d\psi|}{\int_{|\psi(0)\rangle}^{|\psi(T)\rangle} \frac{1}{v_{eff}} |d\psi|} \quad (0.13)$$

where $|d\psi|$ denotes the “length” of an infinitesimal step along the trajectory in Hilbert-space.

The advantage of this special parametrization derives from the fact that the effective velocity

$$v_{eff}^2 = \sum_{i,j} (\dot{\psi}_{ij}^2 + \dot{\psi}'_{ij}^2) = \frac{1}{\hbar^2} \langle \psi(0) | \hat{H}^2 | \psi(0) \rangle \quad (0.14)$$

is constant on each trajectory and thus independent of the time t or the special point on the trajectory. Hence, the integral (0.13) simplifies to

$$\bar{P} = \frac{1}{L} \int_{|\psi(0)\rangle}^{|\psi(T)\rangle} P(\{\psi_{ij}, \psi'_{ij}\}) |d\psi| \quad (0.15)$$

where L is the length of the path. So, the time average of P equals the path average along a special trajectory in this parametrization of Hilbert-space.

We are not able to compute this integral for we do not know \hat{W}' in detail, and even if we did, we could never hope to solve the Schrödinger-equation for a system with about 10^{23} degrees of freedom.

All we want to prove here, is that for typical trajectories staying within the region allowed by the microcanonical conditions, P is extremely close to its minimum value for almost all points within this region.

We proceed as follows:

First we calculate P_{min} which is the smallest possible value of P within the allowed region. Then we compute the average of P over the total allowed region. If this average is close to P_{min} , we can conclude that $P \approx P_{min}$ for almost all points within this region, which means for almost all $P(t)$, since any distribution with a mean value close to a boundary has to be sharply peaked.

From (0.8) it follows that the P_A^g remain conserved. Now the lowest purity P of any state consistent with this condition is:

$$P_{min} = \sum_A \frac{(P_A^g)^2}{N_A^g} \quad (0.16)$$

where N_A^g is the degree of degeneracy of E_A^g .

To calculate the Hilbert-space average of P denoted as $\langle P \rangle$ we need a parametrization for ψ_{ij}, ψ'_{ij} confined to the allowed region (0.9) that essentially consists of hyperspheres in different parts of the Hilbert-space of the total system. The Hilbert-space average can then be written as

$$\langle P \rangle = \frac{\int P(\{\psi_{ij}(\{\phi_n\}), \psi'_{ij}(\{\phi_n\})\}) \det \mathcal{F} \prod_n d\phi_n}{\int \det \mathcal{F} \prod_n d\phi_n} \quad (0.17)$$

where ϕ_n is the respective set of parameters and \mathcal{F} is the corresponding functional matrix.

This integral can actually be solved analytically. The techniques are essentially the same as those used to calculate surface areas of hyperspheres in the classical statistical analysis of the ideal gas. Since this calculation is rather elaborate we do not want to present it in detail here, but give and discuss the result:

$$\begin{aligned} \langle P \rangle = & \quad (0.18) \\ & \sum_A \frac{(P_A^g)^2}{N_A^g} \left(1 - \sum_B (P_B^c)^2\right) + \sum_B \frac{(P_B^c)^2}{N_B^c} \left(1 - \sum_A (P_A^g)^2\right) \\ & + \sum_{A,B} \frac{(P_A^g)^2 (P_B^c)^2 (N_A^g + N_B^c)}{N_A^g N_B^c + 1} \end{aligned}$$

Here N_B^g is the degree of degeneracy of the energy eigenvalue E_B^g .

If the degeneracy of the occupied energy levels is large enough so that

$$\frac{1}{N_A^g N_B^c + 1} \approx \frac{1}{N_A^g N_B^c} \quad (0.19)$$

which should hold true for typical thermodynamical systems, (0.18) reduces to

$$\langle P \rangle \approx \sum_A \frac{(P_A^g)^2}{N_A^g} + \sum_B \frac{(P_B^c)^2}{N_B^c} \quad (0.20)$$

The first sum in this expression is obviously exactly P_{min} (0.16), so that for systems and initial conditions in which the second sum is small the allowed region almost only consists of states for which $P \approx P_{min}$. The second sum will be small if the container system occupies highly degenerate states, typical for thermodynamical systems.

To illustrate this result, we have plotted the relative frequency of P (see Fig 1.), which we calculated using a formula by Lloyd, Pagels [10] and Page [11], that applies to completely degenerate subsystems only. In this case we find from (0.18)

$$\langle P \rangle = \frac{N^g + N^c}{N^g N^c + 1} \quad (0.21)$$

(For this special case the average has also been calculated by Lubkin [12].)

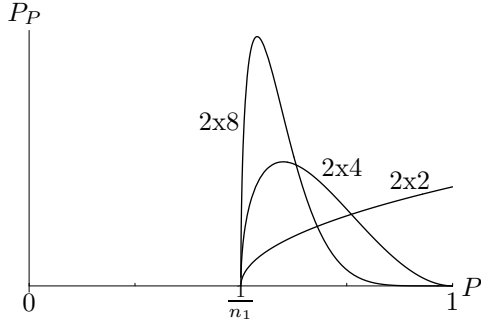


FIG. 1. Probability density as a function of $P = \text{Tr}\{\hat{\rho}_I^2\}$ for various $n_1 \times n_2$ systems. With increasing size of subsystem II the density becomes peaked near the value $\frac{1}{n_1}$.

Obviously our average $\langle P \rangle$ is in perfect agreement with the more detailed distribution of P .

So far we have only shown that, except for negligible parts, the Hilbert-space-section in which the trajectories can be found under microcanonical conditions, has $P \approx P_{min}$, provided the surrounding system is much larger than the considered system.

To examine under what conditions trajectories will even “fill” the whole space they can possibly live in, we consider the special case of no degeneracy in either subsystem. Here the evolution of P can be calculated exactly:

$$P(t) = \sum_{A,B,C,D} e^{\left(\frac{1}{i\hbar}(E_{AB} - E_{CB} + E_{CD} - E_{AD})t\right)} P_A^g P_B^c P_C^g P_D^c \quad (0.22)$$

where E_{IJ} are the energy eigenvalues of the respective energy eigenstates. Note that without any interaction $E_{IJ} = E_I + E_J$ and $P(t) = \text{const.}$, as expected. Assuming that all terms in (0.22) are oscillating except the ones with $A = C$ or $B = D$, we get

$$\bar{P} = \sum_A (P_A^g)^2 + \sum_B (P_B^c)^2 - \left(\sum_A (P_A^g)^2 \right) \left(\sum_B (P_B^c)^2 \right) \quad (0.23)$$

which is exactly the same result as (0.18) with $N_A^g = N_B^c = 1$. So, under this assumption the Hilbert-space average is exactly equal to the time average.

In general, however, this specific ergodicity is not needed: It suffices that typical quantum trajectories, even though starting with $P(0) = 1$, venture out into the vast Hilbert-space regions characterized by $P = P_{min}$. Of course, one cannot exclude that in special situations there might be trajectories that never leave the very tiny region with $P \approx 1$, but these situations become extremely rare as the surrounding gets big.

Finally, we return to the local entropy S . Trying to compute $\langle S \rangle$ rather than $\langle P \rangle$ we get, after some lengthy but straightforward perturbative calculations

$$\langle S \rangle \approx S_{max}(\{P_A^g, N_A^g\}) - K \left(\sum_B \frac{(P_B^c)^2}{N_B^c} \right) \quad (0.24)$$

where K is a positive function that scales linearly with the system size of the gas system. (0.24) is valid for situations with

$$\sum_A \frac{(P_A^g)^2}{N_A^g} \gg \sum_B \frac{(P_B^c)^2}{N_B^c}, \quad (0.25)$$

which is the thermodynamical regime in which the second term in (0.24) will be small. (Again, for the special case of both subsystems being completely degenerate, our results are in perfect agreement with a result by S. Sen [13])

In conclusion we have shown that the local von Neumann-entropy of a considered system will be maximized during its evolution, even if the system is thermodynamically closed, provided the energy eigenspaces occupied by the surrounding are much bigger than the energy eigenspaces occupied by the considered system. This is typical for thermodynamical systems. We did not need the additional assumptions underlying classical derivations. Since we considered microcanonical conditions we get the maximum entropy as an explicit function of the initial energy distribution. This allows for a connection with standard thermodynamics, entropy being a thermodynamical potential.

Generalizations to canonical conditions and the treatment of quantum computer systems as specific open systems are under way.

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